Chapter 17 GASES, Part 2

We've completed several mathematical relationships for the gas phase. Now we'll start putting this into stoichiometry.

17.1 Stoichiometry with gases

As noted in the prior Chapter, we can use the ideal gas equation in stoichiometry. Remember: *PVnRT* provides a link between the number of moles of something and measurable quantities of the sample.

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Example 1. Consider the redox reaction given by the following equation.

$$MnO_2(s) + 4\,H^+(aq) + 2\,Cl^-(aq) \rightarrow Mn^{2+}(aq) + 2\,H_2O(l) + Cl_2(g)$$

You react 4.786 g MnO_2 according to this equation, and you collect all of the chlorine gas in a 458 mL vessel at 19 °C. What is the pressure (in atm) of the chlorine collected under these conditions?

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This is still stoichiometry and it's still the same four Steps which we've been doing. Step 1, the balanced equation, is provided. Proceed to the next Steps.

Step 2. Convert g MnO_2 to mol, using molar mass.

$$\text{g } MnO_2 \rightarrow \text{mol } MnO_2$$

Step 3. Convert mol MnO_2 to mol Cl_2, using rxn ratio.

$$\text{g } MnO_2 \rightarrow \text{mol } MnO_2 \rightarrow \text{mol } Cl_2$$

Step 4. Convert mol Cl_2 to atm Cl_2, using *PVnRT*.

$$\text{g } MnO_2 \rightarrow \text{mol } MnO_2 \rightarrow \text{mol } Cl_2 \rightarrow \text{atm } Cl_2$$

Notice that we are able to make this final conversion to *P* because we have *n* from Step 3 and we have *V* and *T* in the given information.

Although I have been keeping my calculation strings together as much as possible so far, I am going to break this one at the point of entry into the ideal gas equation. I'm doing this for a little added clarity. First, we do Steps 2 and 3.

$$\text{g } MnO_2 \rightarrow \text{mol } MnO_2 \rightarrow \text{mol } Cl_2$$

$$4.786 \text{ g } MnO_2 \times \frac{\text{mol } MnO_2}{86.94 \text{ g } MnO_2} \times \frac{\text{mol } Cl_2}{\text{mol } MnO_2} = 0.05505 \text{ mol } Cl_2$$

So far, this tells us that 0.05505 mol Cl_2 is possible from the reaction. For Step 4, we plug this into *PVnRT*, bringing in the given volume and temperature. Notice that you need to convert temperature to K and volume to L.

$$P = \frac{nRT}{V} = \frac{(0.05505 \text{ mol})\left(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(292 \text{ K})}{0.458 \text{ L}} = 2.88 \text{ atm}$$

That's it.

That's your first taste of stoichiometry with *PVnRT*. Things aren't much different. Let's do another problem, but we'll up the ante.

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Example 2. Consider the reaction of 25.0 mL of 0.561 M ammonium bisulfite solution with excess hydrobromic acid. If all the gas product is collected at STP, what volume (in L) will it occupy?

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This is one of those long, multi-step problems like we did in Chapter 15. Break it into parts. This is stoichiometry and we need a balanced equation. For the balanced equation, we need formulas of reactants and products. You were given names of reactants and you can write the formulas for those. You also need the products. What are they? Well, what kind of reaction is this? You are told a gas is produced. The reactants include a bisulfite and an acid, so the gas is SO_2; a salt and water will also be produced. Which salt? The anion of the salt comes from the acid, so it's bromide. The cation of the salt comes from the other reactant, so it's ammonium. Taken together, the salt is ammonium bromide. Got all that? If so, you can start setting up the equation; if not, go back and review gas-forming reactions in Chapter 12.

$$NH_4HSO_3 + HBr \rightarrow SO_2 + NH_4Br + H_2O$$

That's your equation and it happens to be balanced as written. Step 1 is done.

Now, we head into the stoichiometry string. Again, I'll cut the calculation string for clarity. By the way, the risk involved when you cut the string in the middle is a round-off error. You can avoid this if you don't round-off at the cut. I'll show that here.

Convert L soln to mol NH_4HSO_3 using molarity.

L soln → mol NH_4HSO_3

Convert mol NH_4HSO_3 to mol SO_2 by the rxn ratio.

L soln → mol NH_4HSO_3 → mol SO_2

I'll cut the string here. Run it out to this point.

$$\begin{array}{ccccc} \text{L soln} & \rightarrow & \text{mol } NH_4HSO_3 & \rightarrow & \text{mol } SO_2 \end{array}$$

$$0.0250 \text{ L soln} \times \frac{0.561 \text{ mol } NH_4HSO_3}{\text{L soln}} \times \frac{\text{mol } SO_2}{\text{mol } NH_4HSO_3} = 0.014025 \text{ mol } SO_2$$

We should get three sigfigs out of this stretch, but I didn't round-off yet. Leave this full number on your calculator for the next part.

Now do your final conversion: convert mol SO_2 to L SO_2, using *PVnRT* and the other information which was provided. That completes the path.

L soln → mol NH_4HSO_3 → mol SO_2 → L SO_2

Using the above value of 0.014025 mol, go into *PVnRT*; notice that STP was specified.

$$V = \frac{nRT}{P} = \frac{(0.014025 \text{ mol})\left(0.08206 \frac{\text{L} \bullet \text{atm}}{\text{mol} \bullet \text{K}}\right)(273.15 \text{ K})}{\text{one atm}} = 0.314 \text{ L}$$

After properly rounding, you have your answer: the reaction produces 0.314 L of SO_2 gas.

Alright, another Example. We'll combine a gas mixture problem along with stoichiometry.

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Example 3. The following reaction is conducted at 199 °C in a vessel with a gas volume of 531 L.

$$SiO_2(s) + 4\, HF(g) \rightarrow SiF_4(g) + 2\, H_2O(g)$$

Starting with an initial pressure of 1,142 Torr of HF and with excess SiO_2, what are the pressures (in atm) of SiF_4 and of H_2O at the end? What is the total pressure (in atm) at the end?

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There's a bunch of things here, so you need to break it down. A balanced equation is given, so you don't have to worry about that. You're given an amount for HF. You're told SiO_2 is in excess, so it won't enter into the stoichiometry issue. You're asked for a pressure of SiF_4 and that's one stoichiometry part. You're also asked for a pressure of H_2O and that's a second stoichiometry part. (In the past, we worked a lot with liquid phase H_2O but this time you're told it's a gas by the phase designation in the equation.) The third part of the problem is total pressure, which is just adding the two pressures together. By the way, when you're actually running reactions with more than one gas product, it's the total pressure that determines whether your container blows up or not, so total pressure is a useful calculation.

‣ Part 1. Find the pressure of the SiF_4 product.

Just follow Steps 2 - 4 for general stoichiometry.

Convert the given units for HF into moles of HF. That needs *PVnRT*. I'm plugging 1,142/760 straight into the equation for pressure.

$$n(\text{HF}) = \frac{PV}{RT} = \frac{\left(\frac{1{,}142}{760}\ \text{atm}\right)(531\ \text{L})}{\left(0.08206\ \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(472\ \text{K})} = 20.600...\ \text{mol HF}$$

Convert this to mol SiF_4 by the rxn ratio.

$$20.600...\ \text{mol HF} \times \frac{\text{mol SiF}_4}{4\ \text{mol HF}} = 5.1500...\ \text{mol SiF}_4$$

Notice that I didn't round off yet. We'll round off at the end.

Now, convert this into $P(SiF_4)$ using *PVnRT* and the available information.

$$P(\text{SiF}_4) = \frac{nRT}{V} = \frac{(5.1500...\ \text{mol})\left(0.08206\ \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(472\ \text{K})}{531\ \text{L}} = 0.376\ \text{atm}$$

✓ The pressure of SiF_4 is 0.376 atm. That finishes this part.

‣ Part 2. Find the pressure of the H_2O product.

This starts from moles of HF again, which we already have from Part 1 above: it's 20.600... mol HF. Continuing from there, relate mol HF to mol H_2O by the rxn ratio.

$$20.600...\ \text{mol HF} \times \frac{\text{mol H}_2\text{O}}{2\ \text{mol HF}} = 10.300...\ \text{mol H}_2\text{O}$$

Convert this into $P(H_2O)$ using *PVnRT* and the available information.

$$P(\text{H}_2\text{O}) = \frac{nRT}{V} = \frac{(10.300...\ \text{mol})\left(0.08206\ \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(472\ \text{K})}{531\ \text{L}} = \underline{\hspace{3cm}}\ \text{atm}$$

✓ You fill it in. That's the H_2O pressure.

‣ Part 3. Find total pressure.

This is the bunny part: add the two together.

$$P_{\text{total}} = P(\text{SiF}_4) + P(\text{H}_2\text{O}) = 0.376\ \text{atm} + \underline{\hspace{3cm}}\ \text{atm} = 1.127\ \text{atm}$$

✓ The total pressure is 1.127 atm.

We're done.

This is a good opportunity to show another use of the general gas equation.

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

In the prior Chapter, we used this to derive the pressure/mole ratio relationship for mixtures.

❝ Since everybody's in the same container, $V_1 = V_2$ and $T_1 = T_2$, so the V's and T's drop out.

$$\frac{P_1}{n_1} = \frac{P_2}{n_2}$$

Now, rearrange.

$$\frac{P_1}{P_2} = \frac{n_1}{n_2}$$

This says that pressure ratios and mole ratios are equal between the components within any gas mixture. ❞

For any set of circumstances, as long as $V_1 = V_2$ and $T_1 = T_2$, this relationship holds true. We can even use this in stoichiometry when more than one gas is involved. I'll show this for Part 1 in which we had to find the pressure of the SiF_4 produced from the given amount of HF. Re-arrange the above equation.

$$P_1 = \frac{n_1}{n_2} P_2$$

Set subscript 1 for SiF_4; set subscript 2 for HF. The mol units in the *n*'s cancel out.

$$P(SiF_4) = \frac{1}{4} P(HF)$$

Notice that the mole ratio, 1/4, is the rxn ratio from the balanced equation. Now, plug in *P*(HF) and solve.

$$P(SiF_4) = \frac{1}{4} \times \left(\frac{1{,}142}{760} \text{ atm} \right) = 0.3757 \text{ atm}$$

There's your answer. It's the same as above except for the number of sigfigs.

This method is very general and it can be useful in numerous circumstances. Sometimes it may be faster than the full method which I showed above using our standard stoichiometry Steps 2 - 4. Again, you have multiple methods for doing something. This method can also be used when *T* changes during the reaction, in which case you have to retain T_1 and T_2 in the equation. There are also other variations, but that's enough for us for right now.

This will end our stoichiometry. It's time to change gears.

To this point, we've pretty much emphasized the "big picture", meaning the bulk properties of the gas phase. The bulk properties are the properties of the sample as a whole. Let's go deeper at this time and look at the gas phase more at the molecular level. I've already mentioned some of this in the last Chapter, but now we're ready to see how the bulk properties are related to the molecular behavior.

17.2 Molecules in motion

These three simple words, "molecules in motion", describe a major chunk of the fundamental description of the gas phase. Technically, we refer to the molecular description of the gas phase as the "kinetic molecular theory". "Kinetic" relates to motion anyway, so it's the same thing. But motion isn't the only notion. I'm bringing back the part I said in Chapter 16 for emphasis. It says it more fully.

> ❝ THE MOLECULES OF THE GAS PHASE ARE WIDELY SEPARATED, THEY MOVE RAPIDLY AND RANDOMLY ABOUT, THEIR OWN VOLUME IS VERY LITTLE OF THE ACTUAL VOLUME OF THE SAMPLE, AND THEY DO NOT INTERACT WITH EACH OTHER. ❞

These molecules are whizzing through mostly-empty space, banging into each other or anything else that gets in their way. If they hit one another, they bounce off and go on, although now in some other direction. If they hit something else like the wall of the container they're in, then they bounce off that, too, and bolt off in some other direction. This gives rise to that bulk property which we call pressure. The container feels pressure because the gas molecules are constantly colliding with its walls. If you put a pressure gauge in the sample, the molecules will bang into the pressure gauge and that will register some amount of pressure. What we call pressure is the grand product of all these collisions. This grand product has three parts:

- Velocity. That O_2 molecule in the air just hit you in the eyeball at about one thousand miles per hour. Did you forget to duck? Well, it wouldn't matter. You would never notice it. Although we generally regard a collision at that speed as disastrous, velocity is not the only part of this picture.

- Mass. You would never notice an O_2 molecule hitting you at one thousand miles per hour because its mass is so small, 5.3×10^{-23} g. Even at ten thousand miles per hour, you would not notice anything of that little mass. But mass is not the only part of this picture.

- Frequency. By frequency, I mean the frequency of collision within some area of surface, such as your eyeball or the wall of a container. It's not just one molecule of O_2 colliding with that surface, it's a humongous number of molecules hitting every fraction of a second, constantly. (For 0.21 atm O_2 at 298 K, there're $\sim 10^{23}$ hits per eyeball per second; less if squinting.)

Put all three of these together and you get the bulk property we call pressure: <u>extremely huge numbers of extremely minute masses striking at very high speeds every split second</u>.

These molecules follow the good, old, classical laws of motion, the stuff going back to Newton. (Isaac, not Fig.) These laws deal with mass, velocity, force, etc. With these laws, you can derive *PVnRT*. The derivation ties together the idea of molecules-in-motion with the bulk property of pressure. I won't do the whole thing from scratch right now, but I will derive some of the important results. Our starting point in this discussion is the following equation, using the parameters from above.

$$P = \frac{2}{3} \times \text{mass} \times \text{velocity} \times \text{frequency}$$

Let's look at the terms here. The three in the denominator comes from breaking the motions in three dimensions down to one dimension at a time. The factor of two arises from the physics involved, which relates to the molecule hitting the surface and then bouncing off. The terms mass × velocity give momentum,

$$\text{momentum} = \text{mass} \times \text{velocity}$$

which can be viewed as how hard something hits. This relationship says that heavier and/or faster molecules will hit harder. The frequency is related to velocity and concentration.

$$\text{frequency} = \frac{1}{2} \times \text{velocity} \times \text{concentration}$$

The 1/2 factor arises because, on average in any given sample, half the molecules are moving toward the wall and half are moving away. This frequency relationship says that faster particles will hit a surface more often, and, there will be more total hits per time when there are more molecules per volume. Now we return to the starting equation

$$P = \frac{2}{3} \times \text{mass} \times \text{velocity} \times \text{frequency}$$

and we substitute for the frequency.

$$P = \frac{2}{3} \times \text{mass} \times \text{velocity} \times \frac{1}{2} \times \text{velocity} \times \text{concentration}$$

This simplifies to the following.

$$P = \frac{1}{3} \times \text{mass} \times \text{velocity}^2 \times \text{concentration}$$

We can use n/V for concentration. Let me also abbreviate the other terms: m is for mass and lower case v is for velocity. I'll rewrite this as follows.

$$P = \frac{1}{3} \times m \times v^2 \times \frac{n}{V}$$

We need to bring in a couple more equations, this time dealing with kinetic energy, *KE*. *KE* is just the energy of motion. Laws of motion tell us that, for a single moving object:

(for any object) $$KE = \frac{1}{2} \times m \times v^2$$

A gas sample has many molecules moving at many different speeds. For this, we must derive an average kinetic energy by taking the average of the squares of the speeds for all molecules.

(avg per molecule) $$KE_{avg} = \frac{1}{2} \times m \times \text{avg}(v^2)$$

(Technical point: avg(v^2) means square all the speeds and then find the average of those squares. This is different from first taking the average of the speeds and then squaring that average.) If we consider one mole of these molecules, then the combined mass is one molar mass (here, M).

(for one mole) $$KE_{mol} = \frac{1}{2} \times M \times \text{avg}(v^2)$$

Now, we need one other equation for kinetic energy. This one relates to temperature. It's very important. Although I introduce it last, it is foremost in importance.

(for one mole) $$KE_{mol} = \frac{3}{2} \times R \times T$$

This equation is a biggie: the kinetic energy of a gas sample is determined by temperature only. Notice that R is present. Although R is called the gas constant, it's actually an energy/temperature constant and it comes into play in other applications. I alluded to this in Chapter 16.

> " R is called the gas constant and it will apply for all gases. It's actually a fundamental physical constant which is not just limited to gas things and it pops up in other uses. "

This last equation is the origin of R in *PVnRT*. It's an essential part of the kinetic energy connection. Here's something else to notice in the last equation above: there is no dependence on identity. It doesn't matter at all whether the gas is N_2, O_2, CH_4, H_2O vapor, Xe, or whatever. I'll say it again: THE KINETIC ENERGY OF A GAS SAMPLE IS DETERMINED BY ITS TEMPERATURE ONLY.

Let's continue. Take the last two equations and set them equal.

$$KE_{\text{mol}} = \frac{1}{2} \times M \times \text{avg}(v^2) = \frac{3}{2} \times R \times T$$

Get rid of the halves.

$$\underline{M \times \text{avg}(v^2)} = 3 \times R \times T$$

I underlined a part, but leave the whole equation there for a moment. Bring back pressure from the prior page.

$$P = \frac{1}{3} \times m \times v^2 \times \frac{n}{V}$$

Now convert this equation to mole scale. For one mole, the mass is the molar mass, M. For v^2, we use avg(v^2).

$$P = \frac{1}{3} \times \underline{M \times \text{avg}(v^2)} \times \frac{n}{V}$$

Note that the underlined part here is the same as the part underlined above. Substitute $3 \times R \times T$ for the underlined part.

$$P = \frac{1}{3} \times 3 \times R \times T \times \frac{n}{V}$$

Cancel the 3's and there you have it.

$$P = \frac{n}{V} \times R \times T$$

There's the overall result, just where we started in Chapter 16: the pressure of a gas is proportional to its concentration times its temperature. Here, we see that it all derives from velocity, mass and frequency, as noted earlier in this Section:

> extremely huge numbers of extremely minute masses striking at very high speeds every split second.

And again, this result does not depend on the identity of the gas.

Identity can become important for some parts of this picture. For example, within the term $M \times \text{avg}(v^2)$ for kinetic energy, identity is important due to the molar mass. But, as we see above, this term ultimately drops out to get the usual *PVnRT*. Whenever the mass and speed terms are retained, however, then identity does matter. This leads us to mass and speed relationships for molecules of different substances. This is where we go next.

17.3 The need for speed

Let's go into more detail on molecular speed at this time.

In any gas sample at some typical temperature, some particles are moving fast, some are moving very fast, and some are moving very, very fast. On the other hand, some particles are moving slow, some are moving very slow, and some are moving very, very slow. The particles can also change speed by collision with other particles. Overall, there is a wide distribution of speeds involved. For that reason, when we talk about actual numerical values for speed, we pick a "representative value" for a given set of conditions. There are several forms of "representative values" to choose from; I will go with the simple average speed for our purposes here, designated here as v_{avg}. The calculation for v_{avg}, is the following.

$$v_{avg} = \sqrt{\frac{8RT}{\pi M}}$$

Right away, you can clearly see the connection of speed to temperature and to identity (mass). Before doing an actual calculation, let's look qualitatively at these two important relationships.

First, compare different gases with different molar masses, all at the same temperature.

➻ As M increases, then v_{avg} decreases.

In other words, heavier molecules move slower and lighter molecules move faster. For example, the following is a comparison of increasing molar mass versus decreasing average speed.

molar mass:	H_2 < He < N_2 < CO_2 < SO_2 < Cl_2 < Xe
speed:	H_2 > He > N_2 > CO_2 > SO_2 > Cl_2 > Xe

Xe is heavy and slow. H_2 is light and fast. In fact, H_2 is the lightest and fastest of all gases.

Now let's look at our second qualitative result. Compare the same gas (same M) at different temperatures.

➻ As T increases, then v_{avg} increases.

For any gas, the molecules move faster when the sample is hotter. That carries very important consequences: if the molecules are moving faster, then they are hitting harder and they are hitting more often. That's more pressure!

OK, let's do an actual speed calculation. This is plug-and-chug, using the above equation, but there are two catches to note.

Catch #1. Although R is still the same old gas constant, it does not enter into this equation with the units of L • atm/(mol • K). Instead, we use the following SI units and value for R.

$$R = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

J is the symbol for the SI energy unit called a "joule", homophonous to "jewel". We'll do lots with joules starting next Chapter but, for now, just think of it as an energy unit. This form of R clearly shows R's true nature, which I mentioned upstairs: it's actually an energy/temperature constant and it comes into play in many other applications.

For where we are going, we need to break J completely into its SI base units. That relationship is the following.

$$\text{J} = \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2}$$

Using these units, R is the following.

$$R = 8.314 \frac{\text{kg} \cdot \text{m}^2}{\text{s}^2 \cdot \text{mol} \cdot \text{K}}$$

Catch #2. We need this with g instead of kg so that the mass unit cancels with the mass unit in M in the speed equation. That means we need to use the following version.

$$R = 8{,}314 \frac{\text{g} \cdot \text{m}^2}{\text{s}^2 \cdot \text{mol} \cdot \text{K}}$$

OK, let's go to bottom line: here's the final equation which you need to calculate average speed, with the necessary version of R included.

$$v_{avg} = \sqrt{\frac{8\left(\frac{8{,}314\ \text{g} \cdot \text{m}^2}{\text{s}^2 \cdot \text{mol} \cdot \text{K}}\right)T}{\pi M}}$$

Just plug in T and M and chug away.

Let's do a calculation using those pesky O_2 molecules that keep bouncing off your face. We'll use a typical temperature of 25.00 °C = 298.15 K. O_2 weighs in at 32.00 g/mol. Plug it all in.

$$v_{avg} = \sqrt{\frac{8\left(\frac{8{,}314\ \text{g} \bullet \text{m}^2}{\text{s}^2 \bullet \text{mol} \bullet \text{K}}\right) 298.15\ \text{K}}{\pi\ \frac{32.00\ \text{g}}{\text{mol}}}}$$

Although this is just a plug-in, it's a fairly ugly plug-in. If you squint real hard, you can see that all the units under the square root will drop out except m^2/s^2. (Go ahead, scratch out K's, g's and mol's.) Once you take the square root of m^2/s^2, you get m/s, which is speed. After you plug everything in, punch it out and round it off, you get 444.1 m/s.

Does that seem fast? Not everyone is familiar with metric speeds, so let's convert this to miles per hour. First convert meters to miles and then convert seconds to hours.

$$444.1\ \frac{\text{m}}{\text{s}} \times \frac{\text{mile}}{1{,}609\ \text{m}} \times \frac{3{,}600\ \text{s}}{\text{h}} = 993.6\ \text{mph}$$

That's 993.6 miles per hour and that's fast. Real fast.

Now remember that v_{avg} is a representative speed over all molecules in the sample, but most of the molecules are not moving at that speed. Some of the O_2 molecules might be only going 200 mph and some might be going 2,000 mph. And it can depend on how they hit each other: only through collisions can they change speed (or direction). On the other hand, you can change temperature and start cooking things up, which makes everybody go faster, on average. What say you do the calculation over again?

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Example 4. Calculate v_{avg} for O_2 at 250.00 °C.

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Set it up and plug it in.

$$v_{avg} = \sqrt{\frac{8\left(\frac{8{,}314\ \text{g} \bullet \text{m}^2}{\text{s}^2 \bullet \text{mol} \bullet \text{K}}\right) \underline{\hspace{5em}}\ \text{K}}{\pi\ \frac{32.00\ \text{g}}{\text{mol}}}} = \underline{\hspace{5em}}\ \text{m/s}$$

Compare this speed to the one at 25.00 °C. (Clue: It's 1.3246 times greater.)

The v_{avg} equation provides a useful means to calculate the relative speeds of two different gases (at the same T) as a ratio. For example, let's compare H_2, the world's fastest gas, to O_2, which we just calculated. How much faster is H_2 compared to O_2? First, I'll derive the necessary equation for two gases which are just labeled A and B. Start with the v_{avg} equation.

$$v_{avg} = \sqrt{\frac{8RT}{\pi M}}$$

Write this out for A and for B.

$$v_{avg}(\text{A}) = \sqrt{8RT/\pi M_A} \qquad v_{avg}(\text{B}) = \sqrt{8RT/\pi M_B}$$

Then set up the ratio of the speeds.

$$\frac{v_{avg}(\text{A})}{v_{avg}(\text{B})} = \sqrt{\frac{8RT/\pi M_A}{8RT/\pi M_B}} = \sqrt{\frac{M_B}{M_A}}$$

The $8RT/\pi$ parts cancel out. This leaves the molar mass terms but notice that gas speeds are related by the <u>inverse</u> of the square root of their masses. For comparing H_2 and O_2, we get the following.

$$\frac{v_{avg}(H_2)}{v_{avg}(O_2)} = \sqrt{\frac{M_B}{M_A}} = \sqrt{\frac{32.00\text{ g/mol}}{2.016\text{ g/mol}}} = 3.984$$

This means that H_2 molecules, on average, move 3.984 times faster than O_2 molecules at the same temperature. Since O_2 molecules move ~1,000 miles per hour at 25 °C on average, then H_2 molecules are moving ~4,000 miles per hour at 25 °C. Almost takes your breath away, doesn't it?

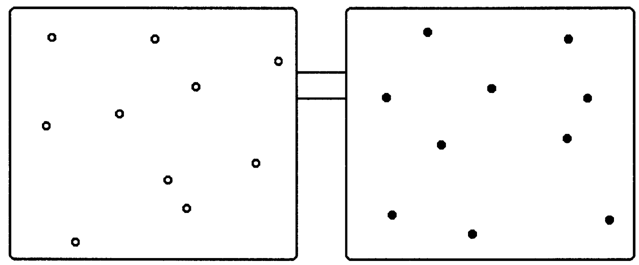
17.4 Diffusion, effusion, deflation and inflation

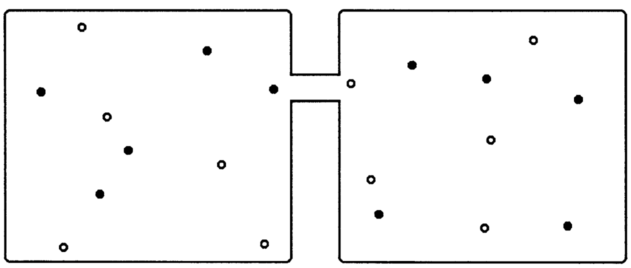
There are other properties and behaviors of gases which are related to their rapid and random motion. I'll describe a few of these.

First, diffusion. As used with two (or more) gases, diffusion is the natural mixing of one gas into another. By "natural", I mean without fans, pumps, etc. It is entirely due to the natural motions of the molecules by themselves. Let me illustrate this.

We start with a container of He and a container of Ne at equal pressures as shown on the right. The atoms of each are moving about within their given volumes.

We then open the connection between the two containers. Both gases are at the same pressure to start, so there's no initial gush from one container to the other.





Over time (at left), atoms of He will fill the full space allowed to them and atoms of Ne will fill the full space allowed to them. They'll mix together and share the same volume. All of this is a natural consequence of their own independent motions. This is diffusion.

Diffusion is a very common occurrence in your world. You know this by smell. Smells are also gases. They obey the same gas laws as N_2 and O_2. Let's say you're sitting in a room somewhere and there are no fans, blowers, etc. moving the air around. Only the molecules of the air are moving themselves around. Then let's say that there's a source of a smell in the room such as perfume, pizza, mothballs, a used baby diaper, or any of two and seventy stenches. The molecules of that smell will get into the air and then do their gas phase thing: they'll move rapidly and randomly, bump into N_2 molecules, bump into O_2 molecules, bump into an Ar atom now and then, etc. Eventually they will diffuse over to your face and get sucked into your nose. In your nose, they do their olfaction reaction, which sends a signal to your brain proclaiming, "I smell!". All of this diffusion business is just another example of molecules in motion. Most smell molecules are a bit heavy compared to air molecules, so that means they'll be slower on average. Molecules of mothballs, for example, with the formula $C_{10}H_8$ and molar mass 128.16 g/mol, are a bit hefty compared to N_2 or O_2, but they'll still get around.

By comparison, liquid solutions can also diffuse but their molecular motions are much more restricted since they are in loose contact. For that reason, diffusion takes much longer. If you place food color at the bottom of a jar of water without stirring and leave the jar sit, then eventually all the water will be colored. That can take many days. For gases in a container of that size, it would be done within minutes.

Another phenomenon which applies for gases is effusion. Unlike diffusion, effusion is not a mixing process. It involves one gas by itself, starting in some container which has a small hole. The hole allows the gas molecules to escape in a somewhat controlled fashion. Some laboratory processes use effusion for studying gases, although these are not as common as they were many years ago. One of its important uses was to measure the molar mass of a gas. Compared to diffusion, the mathematics of effusion is a lot easier. The reason for this is simple: effusion involves the motion of one gas by itself and diffusion involves two (or more) gases mixing together.

Since they sound very similar, it's easy to confuse diffusion and effusion. Just remember that diffusion is mixing and effusion is escaping.

Using effusion to measure molar mass of an unknown gas is fairly straightforward. The process is based on measuring the effusion rate of the unknown and comparing that to the effusion rate of a known gas. Let's say gas A is your unknown and you want to know its molar mass (M_A). You conduct the effusion measurement for A and get its effusion rate. You also do the measurement for a gas you know (gas B) and get its effusion rate. Then you take the ratio of the two rates. This effusion ratio equals the ratio of their speeds, and that ratio was derived above.

$$\frac{\text{effusion rate of A}}{\text{effusion rate of B}} = \frac{v_{avg}(\text{A})}{v_{avg}(\text{B})} = \sqrt{\frac{M_B}{M_A}}$$

Since you know the identity of gas B, then you know M_B; since you measured the effusion ratio, you can use all these things to calculate M_A.

There's another thing about molecules in motion which I'd like to point out, and it is another kind of diffusion. This is not a strictly gas phase process, but I'll mention it here because there is some tie-in. It's a very common experience: balloons. Balloons deflate with time. Well, some inflate by themselves with time, but I'll get to that later. Given the same kind of balloon, a balloon of helium deflates faster than a balloon of air. Why do balloons deflate and why do helium balloons deflate faster?

Molecules in motion. Right through the skin of the balloon. Yes, that's right: gases can pass through many rubber and plastic materials. You can't do that with typical glass or metal containers. Why? It's due to the way the atoms and molecules within the container walls are arranged. In a typical glass or metal, the chemical units are closely arranged and locked in place; nothing can get through. In many rubber and related materials, however, the molecules are extremely long and winding. As such, the molecules do not line up with each other very efficiently. This can leave gaps and channels for something small to sneak through, like a molecule of N_2 or an atom of He. The molecules of a rubber or plastic might also have some wiggle room, and this can open new gaps or even close up some old ones over time.

The deflation of a balloon is another form of diffusion, but this time it involves the mixing of the gas molecules into the balloon material. This is very different from the diffusion of one gas into another gas as mentioned above. This is also much harder to study, and there are several factors which influence the overall process. Some factors depend on the identity of the gas sneaking through and some factors depend on the material of the rubber or plastic. The size of the gas molecule is a big factor: very small gas molecules can get through more gaps than large gas molecules can. The composition of the balloon material will also have an effect because different balloon materials will have different sizes of gaps. The thickness of the balloon skin is yet another factor: thicker balloon skins will take longer to pass through. As you can see, this can be a bit complicated. Curiously, one factor which does not matter much is the mass of the gas molecules. Although mass affects the speeds of gas molecules in a gas phase by itself, mass effects are small for diffusion through a rubber or plastic; size is a much greater issue because everything is in close quarters.

If you have two balloons of the same material and the same thickness, and if one is full of helium and the other is full of air, then the balloon of helium deflates much faster due to size. Monatomic He is the smallest gas particle; air molecules are primarily diatomic N_2 and O_2 and these are significantly larger. To slow things down for He, their balloons are typically made of Mylar or are thicker latex than a common air balloon. Even these deflate with time.

What you may not realize with a helium balloon is that, as it loses helium, it gains air. The passage of gases through a balloon skin can occur in <u>both</u> directions. As helium sneaks out, air sneaks in. Because N_2 and O_2 are much larger than He atoms, however, sneaking in is <u>a lot slower</u> than sneaking out, and the overall effect is still deflation. Nevertheless, some air will still be inside after all He gets out.

Deflation is true in most cases, but not all. I mentioned above that some balloons can inflate by themselves. This is a bit on the weird side since it is not a common experience. Let's talk about a gas with very large molecules, such as sulfur hexafluoride. This is an interesting gas with several interesting applications. For example, it's one of the gases they use in eye operations for repairing some cases of torn retinas: they inject a bubble of it into your eyeball and the bubble helps to hold the retina in place while it heals.

Molecules of SF_6 are very big compared to air molecules. (The molecules also have much more mass compared to molecules of air. Balloons of SF_6 are much heavier than air balloons.) Now think about what I said about helium balloons: the inside gas can sneak out and air molecules can sneak in. In the case of SF_6, the molecules are big clunkers! Air sneaks in faster than SF_6 can sneak out. That means the balloon gets bigger by itself and it can burst from the additional air pressure inside. It's slow, but it does happen.

OK, this concludes our molecules in motion discussion. It's time to move on. Remember: so far, we've been behaving ideally. At least I have. I don't know about those of you snoring out there.

17.5 Reality check

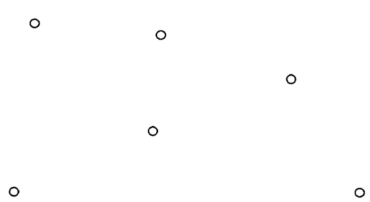
As promised in Chapter 16, we must do our reality check for gases. Actually, under moderate conditions as are typical for Earth surface conditions, the ideal gas properties and all of our equations work fairly well. Under more severe conditions, this won't be the case. Let's see how and why. First, we must return to our basics.

> ❝ THE MOLECULES OF THE GAS PHASE ARE WIDELY SEPARATED, THEY MOVE RAPIDLY AND RANDOMLY ABOUT, THEIR OWN VOLUME IS VERY LITTLE OF THE ACTUAL VOLUME OF THE SAMPLE, AND THEY DO NOT INTERACT WITH EACH OTHER. ❞

This is the description of an ideal gas. On the other hand, parts of that statement are not completely correct over all conditions, and that can cause deviations from ideal behavior. We've talked quite a bit about the wide separation of molecules, the motions of the molecules, and the mostly empty space of a gas, but we haven't said much about interactions between molecules. I will now point out that interactions between molecules can happen and that many of these are attractive. These attractions tend to be weak, especially when the molecules are far apart from each other.

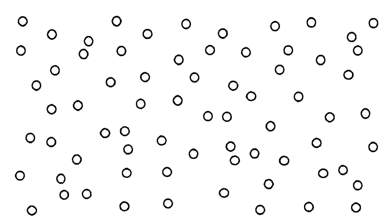
Now, let's see how these things can lead to nonideal behavior.

Much of the problem deals with concentration: ideality is best obtained at low-to-moderate concentrations, while high concentrations tend to deviate more from ideality. Let's compare.



At low-to-moderate concentrations (on the left), the volumes of the molecules remain very small compared to the total volume of the sample and the molecules are indeed widely separated (on average). Since widely separated, they do not significantly interact with each other except during random approaches as they fly around. Under such conditions, the sample behaves ideally.

At high concentrations (on the right), you have a lot more molecules crammed closer together. Now, their own volumes are becoming significant to the total volume. In addition, the molecules are spending more time closer together (on average), and this allows their total interactions to become more important. These conditions can cause a deviation from ideality.



In addition to concentration effects, temperature can also play a role. Temperature has its impact on the interaction part of the story, but this effect is primarily important at temperatures close to the point where the gas would condense to a liquid. (In fact, liquids condense from gases due to these interactions. We'll get into those aspects much more, beginning in Chapter 34.) Near the temperature of condensation, the interactions can cause deviations from ideality. As temperature increases, however, the particles have more energy (on average) and that can override the weak interactions. Thus, as T increases, interactions become less important and the sample behaves more ideally.

Numerous equations have been developed over many years in order to better calculate the real properties of real gases. These equations must now also take into account the specific identity of the gas. Identity is built into these equations because different gases have different sizes of particles and they have different strengths of interaction. One of the historically important equations is the following.

$$\left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT$$

This equation employs adjustments to the pressure and volume terms. *a* and *b* are constants for a specific gas, and they differ for every different gas. Notice that the adjustment to pressure includes a concentration term which, in fact, is squared. There is also a concentration term in the volume adjustment, which is revealed by factoring.

$$(V - nb) = V\left(1 - \frac{n}{V}b\right)$$

I won't go into examples for these calculations. Your instructor may provide values of *a* and *b* for different gases. This equation is decent for not-too-severe conditions. Better equations are available to extend the range of applicable conditions, but these can get more involved. The better equations still incorporate concentration terms and some also include additional temperature terms.

For our purposes right now, this concludes our discussion of the gas phase.

Frequently ideal but always real, these things are part of your world.

Problems

1. True or false.
   a. Both diffusion and effusion are faster at higher temperatures.
   b. At very high concentrations of gases, the volumes of the gas particles can be significant relative to the total gas volume.
   c. For a gas sample at constant *V* and *n*, the pressure increases when the temperature increases because the molecules are hitting harder and more often.
   d. At the same temperature, the gases CO_2 and ClO_2 have the same kinetic energy.
   e. At the same temperature, HCl molecules travel faster (on average) than NH_3 molecules.
   f. Gases deviate more from ideality at lower concentration.

2. The following equation is balanced.

$$2\ SO_2(g) + O_2(g) + 2\ H_2O(l) \rightarrow 2\ H_2SO_4(l)$$

   For a reaction to produce 53.2 g H_2SO_4, what volume (in L) of $O_2(g)$ at STP is required?

3. The following equation is balanced.

$$4\ N_2O(g) + CH_4(g) \rightarrow CO_2(g) + 4\ N_2(g) + 2\ H_2O(l)$$

   The reaction is conducted in a container with a volume of 29.1 L and at 9 °C. The pressure of N_2O is 633 Torr; CH_4 is in excess. What pressure (in Torr) of CO_2 can be produced?

4. How many liters of air at 20. °C and 1.00 atm are needed for the combustion of 50.0 g methyl alcohol, $CH_3OH(l)$, given that the mole percent of $O_2(g)$ in air is 21%?

5. Consider the following balanced equation.

$$2\ H_2S(g) + SO_2(g) \rightarrow 3\ S(s) + 2\ H_2O(g)$$

   The reaction uses 23.1 g H_2S. SO_2 is present in excess; this is supplied from a tank with a fixed volume of 7.00 L and the SO_2 temperature is held constant at 28 °C. The initial pressure of SO_2 is 3.19 atm. What is the final pressure (in atm) of the remaining SO_2 after the reaction is done?

6. The following compounds are solely or partly responsible for various common smells. Rank the compounds by how fast (slowest to fastest) their smells will diffuse through a room (at the same temperature).
   a. $C_6H_{10}S_2O$ (garlic) b. C_4H_8S (skunk) c. $C_{10}H_8$ (mothballs)
   d. $C_{10}H_{20}O$ (menthol) e. CH_3CO_2H (vinegar)

7. What is the average speed (in m/s) for $H_2O(g)$ at 25 °C?

8. What is the average speed (in m/s) for $H_2(g)$ molecules at 24 °C?

9. An effusion measurement is done on an unknown gas. Relative to the effusion of N_2 under the same conditions, the ratio of the effusion rates (unknown/N_2) was 0.565. What is the molar mass of the unknown gas?